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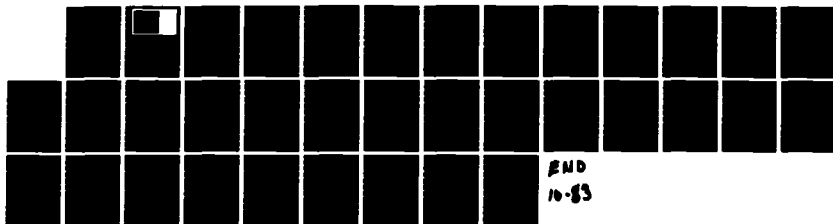
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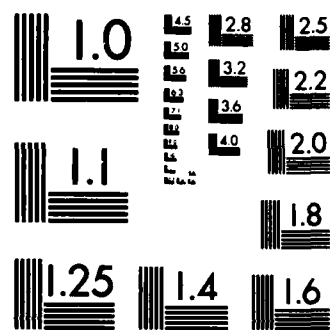
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MRC Technical Summary Report #2537

NOTE ON EVAPORATION IN CAPILLARIES

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MATHEMATICS RESEARCH CENTER

NOTE ON EVAPORATION IN CAPILLARIES

R. E. Meyer

Technical Summary Report #2537
July 1983

ABSTRACT

Factors are discussed which govern evaporation of liquid in small capillaries of greatly varying bore, such as might be encountered in porous media. If the escape of the vapor is relatively unobstructed, marked temperature gradients are found to be confined to close neighborhoods of the menisci. Evaporation is shown to proceed in statically unstable configurations under a dynamic balance of surface tension, local evaporation rate and viscous shear. The larger capillary throats clear first, the smallest ones remain full of liquid. Evaporation rates and fluid velocities are determined approximately.

AMS (MOS) Subject Classifications: 76S05, 80A20

Key Words: menisci, capillary throats, porous media

Work Unit Number 2 (Physical Mathematics)

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SIGNIFICANCE AND EXPLANATION

An electric dryer is not always to hand when liquid needs to be extracted from clothing. That raises the question what physical factors govern evaporation in a fabric under unfavorable circumstances and then, what a knowledge of the physical process might tell us about expedients that would help to control it in a more advantageous way?

To make a start in this direction, the following investigation studies evaporation in a porous medium of which the void consists of an irregular network of small capillaries. The nature of the process is found to differ markedly from what is plausible without closer analysis, and the way in which various geometrical and physical parameters combine to control it is elucidated.

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The responsibility for the wording and views expressed in this descriptive summary lies with MRC, and not with the author of this report.

NOTE ON EVAPORATION IN CAPILLARIES

R. E. Meyer

1. INTRODUCTION

Most outdoor enthusiasts can recall the dismal experience of donning cold, wet clothes after a night in a tent. The study here reported was prompted by such a physicist, who pointed out that little appears known about the factors governing the drying process inside fabrics beyond the simple guess that the rate of heat supply to the fabric may equal the rate of latent-heat expenditure in it.

As a first step towards learning more, it seemed helpful to think of a porous medium forming an irregular network of interconnecting, small capillaries along each of which the capillary bore varies by a large factor. It also appeared wise to avoid the difficulties associated with the peculiar shape of fabric capillaries for this first study and instead, think in terms of 'equivalent circular' capillary cross-sections. Thought then turns naturally to evaporation in a single capillary and thence, to further division of the difficulties by isolating some of the interacting, physical processes in order to clarify them separately and to learn thereby to distinguish the factors which might govern evaporation from those which really do.

The main, dividing step will be to borrow from the fabric the notion of a 'sheet-like' porous medium in which evaporation occurs mainly at menisci whence the vapor can escape without hindrance. That serves to postpone any consideration of processes in the air-vapor mixture to Section 6. It also amounts, in effect, to adoption of the simple form

Sponsored by the United States Army under Contract No. DAAG29-80-C-0041 and partly supported by the National Science Foundation under Grant No. MCS-8215064.

Heat supply = latent-heat expenditure
of the First Law in order to explore its implication for the local processes
and then, in turn, establish the conditions under which that form of the First
Law applies to porous media (Section 6.2).

Road forks are next encountered in the consideration of the manner of
heat supply, and the array of alternatives threatens to preempt the
foreground. Since heat transfer between solid and fluid tends to be important
in any case, the path here chosen will be to envisage the heat as reaching the
fluid from the solid. This is made specific enough in Section 3.2 to get the
discussion going and, once results are to hand, it becomes easier to see
(Section 4.2) why most of the roads not taken converge to the same
destination.

The liquid then remains in the foreground, and consideration will be
given first to a situation of idealized symmetry (Sections 3.4 to 4.2) that
eliminates the interaction between different menisci. It should probably not
have surprised the Author to find (Section 4.2) that the thermal process is
then a very local one confined to less than a capillary bore's distance from
the meniscus. A serious analysis of this process depends on contact angles
and thermal properties of the solid to a degree placing it beyond the scope of
this Note, but an estimate of the evaporation rate at a meniscus emerges none
the less (Section 4.2).

It shows promptly that the assumed symmetry is unstable (Section 5.1)
because evaporation retracts a meniscus into the liquid at a speed inversely
proportional to the meniscus size: Two equal menisci bounding a liquid column
therefore interact to make one grow smaller than the other! The imbalance of
surface tension then sets the liquid in motion, and a dynamic balance of
surface tension and viscous shear emerges (Section 5.2) which illuminates the

nature of evaporation in irregular capillary networks (Section 7): The smallest menisci remain almost stationary near the smallest capillary throats, while most of the evaporation occurs at the large menisci and clears, by and by, all the larger capillary throats.

The present investigation differs from earlier ones [1-3] by concentrating on the local, "microscopic" processes, and its results indicate a strong dependence of the very nature of fluid processes in porous media on the specific structure of the medium and in particular, on the distribution of capillary throat sizes. One reason for this is that pressure differences are localized at menisci and at capillary throats, and a factor 10^{-1} in the local bore there corresponds to a factor 10 in pressure difference across a meniscus (Section 1), but 10^4 , across a throat (Section 5).

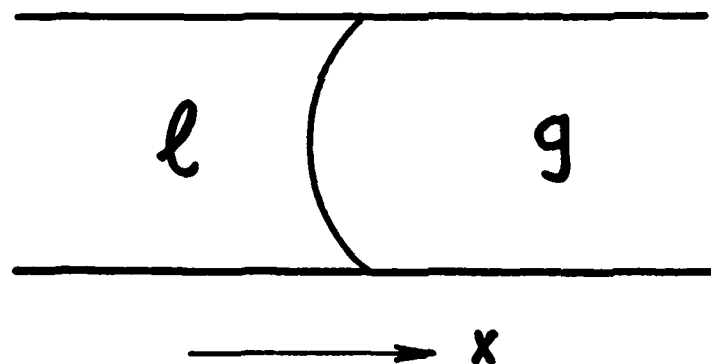


Figure 1

2. STATIC EQUILIBRIUM

The liquid will be assumed to wet the capillary wall, i.e., the meniscus is curved so that the pressure on the gas side exceeds that on the liquid side,

$$P_g = P_l + 2\sigma/a_M, \quad (1)$$

where a_M denotes a mean radius of curvature of the meniscus. If a body of liquid has a boundary containing two menisci of different curvature and if the gas pressure is the same at both, then (1) implies a pressure gradient driving the liquid towards the smaller meniscus. Body forces are not of great importance in the present context and will be ignored. The wetting assumption is therefore necessary for spontaneous penetration of liquid into the porous medium.

It has also decisive implications on the configuration that a liquid mass can have in a porous medium before evaporation begins. Suppose first that the liquid occupies a connected segment of a single capillary and that the gas pressure is the same at both ends of this liquid column. Static equilibrium then requires menisci of the same size a_M at both ends. Such an equilibrium is stable, moreover, if and only if the capillary radius $a(x)$ increases at both menisci in the direction towards the gas.

The same consideration carries to a porous medium envisaged as an irregular network of many interconnected capillaries. If the gas pressures are the same at all the menisci, it follows again from (1) that a liquid configuration corresponds to a stable, static equilibrium if, and only if, all the menisci are of the same size and in positions at which the capillary radius increases towards the gas. The initial position, before evaporation, of a connected, liquid drop must satisfy this condition, and the void domain in the porous matrix which the drop fills must therefore be of a very irregular shape characterized by the tendency of the liquid to fill smaller capillary throats in preference to larger ones.

Evaporation, of course, threatens to upset such equilibria because a decrease in the liquid mass must soon retract some meniscus through a capillary throat. Its position then becomes statically unstable, and the

whole liquid mass must move in a "Haines Jump" [1] to seek out a new, stable configuration. On kinematic considerations, such jumps would be expected to be very frequent and evaporation, to be a continuous process only on a long-term average [2]. It may come as a surprise to some readers that thermodynamics and dynamics rules out staccato jumps during evaporation in an irregular network with enough small capillary throats (Section 7) and in fact, shows the liquid then to be not in static equilibrium at all (Section 5.2).

3. BALANCES

3.1. Phase Equilibrium

Since the surface tension acts towards the vapor, it also promotes evaporation. Helmholtz' analysis [4, p. 436] of equilibrium between the liquid and air-vapor phases at a curved interface treats the air-vapor mixture as a perfect gas and predicts a ratio

$$p_{gM}/p_g = \exp(-He) < 1$$

of the local pressure p_{gM} on the gas side of the meniscus to the standard gas pressure at the same temperature above a flat liquid surface. The Helmholtz number is

$$He = 2\sigma/(a_M \rho_l R_g T) = 2\sigma \rho_g / (a_M \rho_l p_g)$$

where ρ , R and T denote respectively density, gas constant and absolute temperature, while subscripts l and g will be used throughout to distinguish reference to the liquid and gas phases.

To fix the ideas, this study will envisage roughly atmospheric pressures, temperatures in the atmospheric and body ranges, and liquids of physical properties similar to those of water. Typical values of surface tension and density ratio are then $\sigma = 0.075$ g/cm and $\rho_g/\rho_l = 10^{-3}$, respectively, and for mean meniscus radii $a_M = 10^{-5}$ (10^{-4}) cm, the Helmholtz number is about

$10^{-2}(10^{-3})$, and the interface curvature effect on evaporation is therefore insignificant in the present context.

Like Helmholtz' analysis, the present study will be based on equilibrium thermodynamics. The temperature is then continuous at the meniscus and its local value there will be denoted by T_M . During evaporation, the gas there must be at the "dew point", where the partial vapor pressure p_{VM} is the saturation pressure,

$$p_{VM} = p_{\text{vsat}}(T_M) .$$

For water vapor, e.g., $p_{\text{vsat}} \approx 1/40(3/40)$ atm at $T_M \approx 293(313)^{\circ}\text{K}$, and the gas even at the meniscus then consists almost entirely of air.

3.2. Ambient Conditions

Consideration of the process in the gas may be postponed to Section 6 by the expedient of confining attention first to capillaries in which the escape of the vapor is unobstructed. Pressure differences in the gas, and the work needed to move the vapor out of the capillary, are then insignificant, and the gas pressure p_g may be taken to be a given ambient pressure p_0 . To fix the ideas, it may be assumed atmospheric.

Evaporation requires a supply of latent heat to the meniscus and could not be maintained for long, if it depended on heat stored initially in the porous medium. Prolonged evaporation must therefore be fuelled by an external heat supply and may depend on the rate and manner of that supply. The immediate need, however, is for a framework specific enough to support discussion of the process near individual menisci without ignoring heat transfer between solid and fluid. To fix the ideas, then, it will be envisaged that an external reservoir supplies the heat to the solid, in the first place. More specifically, the whole medium will be assumed originally

at rest and at a known, uniform temperature T_0 , with the gas saturated at the ambient pressure p_0 . The solid was then heated gradually so as to raise its temperature far from the capillary wall to a level at which it is maintained by the external supply. This does not imply a temperature field constant in time or uniform in space, because evaporation makes menisci act like moving heat sinks of strength changing with time. The properties of the solid, however, are outside the scope of this study and, on the assumption that they are uniform, the capillary wall temperature will emerge in Section 4.2 to vary remarkably little over most of the capillary length. The stronger variation near menisci, moreover, can be accounted for approximately by rough adjustments (Appendix). That suggests regarding the capillary wall itself as a reservoir supplying heat at a temperature T_w , say. Local evaporation estimates in terms of T_w will be obtained in the following sections and it will be indicated briefly in Section 7 how T_w may be expected to be determined by the external heat-supply rate and the distribution of capillary sizes in a porous medium.

3.3 Meniscus Balance

Since the liquid and gas at any meniscus are envisaged in dew-point equilibrium to begin with, and since the gas pressure there remains at the ambient level p_0 until Section 6.2, any heat reaching the meniscus will result in evaporation, but not [3, p. 45] in a change of the local temperature T_M from its original level T_0 .

The fluid temperatures away from the meniscus, on the other hand, will be raised above T_0 by transfer of heat from the capillary wall, and this will lead to a supply of heat to the meniscus by conduction through the fluid. Its description will be simplified greatly by representing quantities in the fluid

by their averages over a capillary cross section and ignoring the errors resulting from employment of somewhat different averages in different contexts. The local temperatures in the liquid is then represented by its average T_ℓ dependent only on time t and distance x along the capillary. On this model, conduction through the liquid in $x < \ell$ contributes heat to a meniscus at $x = \ell(t)$ at the rate

$$-\pi a_m^2 \lambda (\partial T_\ell / \partial x)_{x=\ell},$$

where λ denotes the coefficient of heat conduction of the liquid and a_m , the capillary radius $a(\ell)$ at the meniscus. Conduction through the gas in $x > \ell$ does not contribute comparably (because its heat conductivity is smaller), and its neglect constitutes one of the many minor errors of which the estimates do not merit space here.

A more significant omission of the model is its neglect of meniscus curvature. If that is marked, there is a short capillary segment in which heat reaches the meniscus by direct transfer across the wall and radial conduction in the liquid, rather than by the axial conduction so far accounted for. A realistic model of heat transfer requires consideration of thermal properties of the capillary wall, which threatens to lead off on a tangent. For immediate purposes, it appears preferable to lump them into the most rudimentary, conventional model of a heat transfer rate per unit wall area proportional to the temperature difference $T_w - T_\ell$ with a constant coefficient h . If $a_M/a(\ell) = \alpha_1$, then the area of capillary wall from the meniscus contact line to the position of the meniscus apex (Figure 1 above) is approximately $2\pi a_m^2 \alpha_2$ with $0 < \alpha_2 = \alpha_1 - (\alpha_1^2 - 1)^{1/2} < 1$. The rate of heat transfer across this wall segment is then

$$2\pi a_m^2 \alpha_2 h_M (T_w - T_M),$$

where h_M denotes a value of the transfer coefficient h adjusted (Appendix)

to compensate for the error made by ignoring that the wall temperature at the meniscus differs from its general level T_w .

Consider now a short capillary segment S of fixed length which is stationary in a frame moving with the local, liquid velocity and which contains the meniscus at this time. The gas pressure and the temperature are constant in it. If Dl/Dt denotes the velocity of the meniscus in that frame, the mass-rate of evaporation in S is

$$m = -\pi a_m^2 \rho_g \frac{Dl}{Dt} . \quad (2)$$

The mass of gas in S is not increasing at a significant rate because ρ_g/ρ_l is very small, and vapor therefore leaves S at the same mass-rate m . Since no liquid enters S , the net rate of mass loss in S is also m , and the corresponding, net rate of enthalpy gain is $-mi_g$. By the First Law, that equals the rate of heat addition by transfer and conduction into S less the rate mi_v of vapor enthalpy leaving S ,

$$\pi a_m^2 [2 \alpha_2 h_M (T_w - T_M) - \lambda \partial T_g / \partial x] = m L \quad (3)$$

because the specific enthalpy difference $i_v - i_g$ is the latent heat L per unit mass.

3.4. Liquid Balance

The thermal description of evaporation is greatly simplified if no liquid motion couples the processes at different menisci. Such a description is possible in the idealized case of a capillary of radius $a(x)$ even in x , if the temperature field is similarly even and liquid fills a capillary segment between menisci at $x = \pm l$, with $a'(l) > 0$. The evaporation processes at the two menisci are then mirror images of each other and there is no liquid velocity at $x = 0$, nor anywhere else, by mass conservation, if the minor dependence of liquid density on temperature be ignored. The symmetry of the

process can continue in principle, and also in practice, if its static stability (Section 2) be accompanied by thermodynamic stability (Section 5.1). Such symmetry will be assumed for the remainder of this section and for Section 4.

With the same, rudimentary model of heat transfer as just used for the meniscus balance, the local thermal balance per unit length of capillary is then

$$\pi a^2 \rho_l c_l \frac{\partial T_l}{\partial t} = \frac{\partial}{\partial x} \left(\pi a^2 \lambda \frac{\partial T_l}{\partial x} \right) + 2\pi a h (T_w - T_l) .$$

It is an insignificant further approximation to neglect variations in λ , ρ_l and the liquid heat capacity c_l , and the balance then becomes

$$\frac{\partial T_l}{\partial t} = \frac{\kappa}{a^2} \frac{\partial}{\partial x} \left(a^2 \frac{\partial T_l}{\partial x} \right) + \frac{2 h}{\rho_l c_l a} (T_w - T_l) , \quad (4)$$

where κ denotes the usual heat diffusivity,

$$\kappa = \lambda / (\rho_l c_l) .$$

The liquid therefore experiences a typical heat conduction process with variable, effective diffusivity and heat transfer, but because of the symmetry, without convection.

4. SYMMETRIC EVAPORATION

4.1. Thermal Length Scale

One of the difficulties in drawing conclusions from such balances, as Prandtl taught us, is the a-priori uncertainty whether a single set of length, time and temperature scales can be representative of the temperature field throughout the liquid column. One may agree, however, to restrict attention to any one subsegment of the column short enough for such a representation and let X , τ and Δ denote the respective length, time and temperature-

difference scales there. Even without attention to the cross-sectional shape, the capillary geometry is described by two functions, $a(x)$ and $a'(x)/a(x)$ of normally different order of magnitude in a porous medium, and attention may need to be restricted further to any one subsegment such that a single radius scale a_0 and a single length scale G are there representative of $a(x)$ and $a(x)/a'(x)$, respectively. By contrast to these geometrical scales, X denotes the length scale of the temperature variation in the same subsegment.

If now a , a/a' , x and t are measured in the respective units of a_0 , G , X and τ , and if

$$T_w - T_\ell(x,t) = T(x,t) \Delta,$$

then the local thermal balance (4) becomes

$$\frac{1}{\kappa\tau} \frac{\partial T}{\partial t} - \frac{2a'/a}{G X} \frac{\partial T}{\partial x} = X^{-2} \frac{\partial^2 T}{\partial x^2} - \frac{1}{\Lambda^2 a} T \quad (5)$$

where now T , t , x and $a(x)$ are nondimensional and "of order unity", as are the derivative of $T(x,t)$, and

$$\Lambda = \left(\frac{1}{2} \lambda a_0 / h \right)^{1/2}$$

is a thermal length scale of decisive significance. Independently of the heat transfer model, the product $2\pi a_0 h \Lambda$ represents the scale of heat transfer rate into unit length of liquid column. The scale of heat diffusion rate into, or out of, the same length of liquid column is $\pi a_0^2 \lambda \Delta / X^2$, and so Λ^2 / X^2 represents the ratio of the diffusion scale to the transfer scale.

While the coefficient h in (6) refers to the particular, rudimentary model of transfer, any other model must also end up defining an analogous scale Λ . For the particular model, it is a global property of any capillary segment characterized by a single radius scale.

To obtain some guidance on how this thermal length Λ compares to the other length scales, a somewhat more detailed calculation of heat conduction and transfer is sketched in the Appendix. It indicates that Λ should be anticipated to be of the order of the capillary radius a , at most!

Accordingly,

$$\Lambda/a_0 = [\lambda/(2a_0h)]^{1/2} = \gamma_h \quad (6)$$

will be regarded as a parameter of order unity in what follows. A rough estimate of its numerical value will be needed occasionally, and the Appendix indicates $\gamma_h = \frac{1}{2}$ to be a reasonable, rough approximation.

4.2. Slow Evaporation

In a porous medium, the bore of a capillary might vary greatly over its length. It is then helpful to confine attention first to a segment adjacent to the initial meniscus position $l(0)$ and short enough to be characterized by a single radius scale a_0 . Since the thermal scale Λ is of the same order and the geometric scale G of $a(x)/a'(x)$ cannot plausibly be expected to be shorter, a_0 is then the scale on which the thermal process needs elucidation first.

Accordingly, the scale X in (5) will now be identified with a_0 , so that this balance becomes

$$\frac{a_0^2}{\kappa T} \frac{\partial T}{\partial t} - \frac{2a'}{a} \frac{a_0}{G} \frac{\partial T}{\partial x} = \frac{\partial^2 T}{\partial x^2} - \frac{1}{\gamma_h^2 a} T. \quad (7)$$

The natural temperature-difference scale for such a capillary segment is

$T_W - T_M = \Delta$, and in these units,

$$T(l, t) = 1$$

at the meniscus, and the meniscus balance (3) reads

$$\left. \frac{\partial T}{\partial x} \right|_{x=l} + \frac{\alpha_3}{\gamma_h} = - \frac{a_0^2}{\epsilon \kappa \tau} \frac{dl}{dt} ,$$

by (2) and since the liquid is now at rest; here l is now also referred to the unit a_0 , $\alpha_3 = \alpha_2 h_M / h$ and

$$\epsilon = c_l \Delta / L .$$

In the circumstances motivating this study, it is implausible that the capillary wall could be heated up so that $\Delta = T_W - T_M$ becomes comparable with L/c_l , and therefore,

$$\epsilon \ll 1 .$$

For water, e.g., $\Delta = 50^\circ\text{F}$ corresponds to, roughly, $\epsilon = 1/20$.

Two time scales therefore emerge in these balances, of which the scale $\tau_t = a_0^2 / \kappa$ characterizes transients arising from an imbalance of heat transfer and conduction. It would normally be expected to be a rather small fraction of a second, for instance, if $\kappa = 10^{-3} \text{ cm}^2/\text{sec}$ and $a_0 = 10^{-2} \text{ cm}$, then $\tau_t = 10^{-1} \text{ sec}$. The motion of the meniscus, by contrast is characterized by the time scale

$$\tau_l = a_0^2 / (\kappa \epsilon) ,$$

which is much longer. A question of primary interest is whether a relatively stable evaporation process is possible and what its nature would be? The most helpful approach to this is to examine the balances for such a solution first, and to this end, t will now be measured in units of τ_l .

Even in porous media, the length scale G of changes in capillary bore will normally be large compared with the bore, so that $a_0/G \ll 1$, and the lefthand side of (7) becomes unimportant by comparison with the righthand terms, in which $a^{-1} \approx 1$, to the same approximation. That reduces the balances to

$$\partial^2 T / \partial x^2 = \gamma_h^{-2} T$$

$$T(l, t) = 1,$$

$$\partial T / \partial x \big|_{x=l} + \gamma_h^{-2} \alpha_3 = -dl/dt,$$

of which the solution is

$$T = \exp \frac{x - l(t)}{\gamma_h}, \quad l(t) = l(0) - \frac{\gamma_h + \alpha_3}{\gamma_h^2} t. \quad (8)$$

It describes a very short meniscus layer, of thickness equal to the thermal length scale $\Lambda = \gamma_h a_0$, in which virtually the whole process of heat transfer to, and heat conduction in, the liquid takes place.

This result destroys a premise of the discussion: the thermal layer is of thickness comparable to the meniscus depth, so that the liquid temperature averages have been taken over cross-sections not filled with liquid. The heat transfer and conduction process generating the evaporation cannot therefore be discussed independently of the meniscus shape, but little is known presently on contact angles [5], and any less speculative calculation must also account for the temperature field in the solid. On the other hand, there can be no doubt that a correct analysis of the process would involve the same dimensional groups, so that the dimensional velocity of the meniscus relative to the liquid is

$$\gamma \frac{\kappa \epsilon}{a_0} = \gamma \frac{\lambda (T_W - T_M)}{a_0 \rho_L L},$$

as indicated by (8), and the dimensional evaporation time for a capillary segment l_0 is

$$\gamma^{-1} l_0 a_0 / (\kappa \epsilon).$$

What has no rational support is the value $\gamma = (\gamma_h + \alpha_3) / \gamma_h^2$ of the nondimensional coefficient γ predicted by (8). Attaching a rough, numerical

value to it will, however, help greatly in fixing the ideas, and since

$0 < \alpha_2 < 1$ and $0 < h_M/h < 1$, $\alpha_3 = \alpha_2 h_M/h$ cannot differ too much from $1/2$ and the value $\gamma_h \approx 1/2$ of the Appendix suggests

$$\gamma \approx 4,$$

although there has certainly been no reason adduced here for preferring that number to 3 or 5. It may help also to quote rough numbers for water

($\kappa = 0.0014 \text{ cm}^2/\text{sec}$) and $\epsilon = 1/20$; then various capillary radii give roughly the following meniscus velocities and evaporation times:

TABLE 1

| | | | | | | |
|-------------------------------|--------------------|--------------------|-----------|--------------------|--------------------|--------|
| a_0 | 10^{-2} | 10^{-3} | | 10^{-4} | | cm |
| $4\epsilon\kappa/a_0$ | 3×10^{-2} | 3×10^{-1} | | 3 | | cm/sec |
| l_0 | 10^{-1} | 10^{-1} | 10^{-2} | 10^{-2} | 10^{-3} | cm |
| $l_0 a_0 / (4\epsilon\kappa)$ | 3 | 1/3 | 1/30 | 3×10^{-3} | 3×10^{-4} | sec |

The preceding discussion applies, in the first place, to the capillary segment which ends at the initial meniscus position and is characterized by a single scale of capillary radius. Once the meniscus has traversed it, however, the same discussion resumes with a different value of a_0 . The dependence of γ_h on a_0 in (6) arises only from the notation chosen for the heat transfer. The meniscus velocity therefore varies in inverse proportion to the capillary bore, and unless narrower segments are very much longer, their evaporation time is much shorter. For the symmetrical evaporation, of

course, the innermost segment must satisfy the additional condition

$\partial T / \partial x = 0$ at $x = 0$, so that (8) is there replaced by

$$T(x,t) = 2 e^{-l(t)/\gamma_h} \cosh(x/\gamma_h) .$$

The initial warming of the liquid is unlikely to occur on a time scale shorter than τ_l , and the main cause for rapid transients on the scale τ_t would therefore be expected to be static instability causing "Haines jumps" (Sections 2, 5.2).

The main result found so far, namely that evaporation at a meniscus is associated with only local temperature gradients, implies that the manner of external heat supply has less influence upon it than might have seemed plausible. First, since the ratio of capillary volume to surface area decreases in proportion to bore size, heat transfer across capillary walls must, in any case, play an important role in the distribution of the supplied heat through the porous medium. The resulting distribution of heat, secondly, must be on a length scale reflecting the dimensions of the porous medium. On the much smaller scale of the thermal meniscus-layers, the ambient temperature background then appears effectively uniform.

For instance, if body heat fuels evaporation, then the main feature added to the estimates would be expected to be that the ambient temperature level T_w and hence, also the parameter $\epsilon = c_l (T_w - T_0) / L$, depend on distance from the surface of the porous medium.

5. ASYMMETRIC EVAPORATION

5.1. Instability.

The symmetrical capillary model has served to isolate and clarify the thermal process in the liquid, but it is quite unrealistic in the context of a

porous medium. Initially, all the menisci must be of equal size (Section 1) but that is not certain to persist during evaporation. Indeed, even if there be another time at which two menisci bounding a liquid column are of equal size and the liquid is at rest, so that the menisci then move into it with the same evaporation velocity, it could happen rarely that $a'(x)$ then also takes the same value at both menisci: Normally, the radii of the two menisci would therefore not change at the same rate. Surface tension acts to redress this by a motion of the liquid, but evaporation makes the smaller meniscus move faster relative to the liquid. Which will win?

Consider then a configuration in which the capillary bores differ at the two menisci bounding a liquid column, but which does not call for a "Haines jump": $a'(x)$ is monotone increasing over the whole column, which fills a capillary segment containing a throat. Assume, as before, that the temperatures and gas pressures are the same at both menisci. Denote their positions by $x = l_+$ and $x = l_- < l_+$, respectively, and for definiteness, let the capillary radii there be $a(l_+) = a_+$ and $a(l_-) = a_- < a_+$, i.e., the smaller meniscus is at the lefthand end of the liquid column. By (1), the liquid-pressure difference is then

$$p(l_+) - p(l_-) = \frac{2\sigma}{\alpha_1} \frac{a_+ - a_-}{a_+ a_-},$$

where $\alpha_1 = a_m/a_m$ denotes again the ratio of the meniscus radius to the local capillary radius.

For simplicity, suppose the resulting liquid motion to be steady and the capillary radius $a(x)$, to change slowly with distance x , then a good approximation to the relation between pressure and mass-flow rate Q in the direction of x increasing (i.e., towards the right) is given by Poiseuille's formula,

$$Q = - \frac{\pi \rho}{8\mu} a^4 \frac{dp}{dx},$$

and mass conservation makes Q independent of x . Neglect liquid density variations, then

$$p(l_+) - p(l_-) = - \frac{8\mu Q}{\pi \rho} \int_{l_-}^{l_+} [a(x)]^{-4} dx$$

and the main contribution to the integral arises from the part of the capillary near the throat. If the throat radius is a_t , the integral may be written l_t/a_t^4 in terms of a "throat length" l_t , and

$$p(l_+) - p(l_-) = -8 \mu Q l_t / (\pi \rho a_t^4).$$

The mass-flow rate caused by surface tension is therefore

$$Q = - \frac{\pi \rho \sigma}{4\alpha_1 \mu} \frac{a_t^4}{a_+ a_-} \frac{a_+ - a_-}{l_t},$$

and the corresponding cross-sectional averages of liquid velocity are $Q/(\pi \rho a_+^2)$ at the right meniscus and $Q/(\pi \rho a_-^2)$, at the left one.

Evaporation has been seen in Section 4.2 to retract the menisci into the liquid with velocities $\gamma \kappa \epsilon / a_+$ and $\gamma \kappa \epsilon / a_-$, respectively. As long as a_+ and a_- do not differ much, the rate at which the liquid column shortens is therefore not changed greatly by the liquid motion. The rate at which the center of the liquid column shifts, however, is now

$$\frac{d}{dt} \frac{l_+ + l_-}{2} = \frac{\kappa \epsilon}{2} \frac{a_+ - a_-}{a_+ a_-} \left[\gamma - \frac{1}{4\alpha_1 Ce} \left(\frac{a_t^2}{a_+ a_-} \right)^2 \frac{a_+^2 + a_-^2}{a_0^2 l_t} \right],$$

where

$$Ce = \epsilon \kappa \mu / (\sigma a_0)$$

is a capillary number based on the evaporation velocity scale and may be expected to be small; for water, e.g., $4a_0 Ce \sim 10^{-8}$ cm. The factor of Ce^{-1}

in the bracket, however, is very small as long as a_+ and a_- remain large compared with the throat radius a_t . During such a phase of evaporation, the liquid column therefore shifts towards the side of the larger meniscus! The symmetrical configuration envisaged in the preceding section is therefore unstable under evaporation.

If the smaller meniscus were found close to the throat, on the other hand, then the second term in the last bracket would be large and the liquid column shifts towards the side of the smaller meniscus, which then moves away from the throat.

In sum, surface tension is seen to prevent either meniscus from passing through the throat, in the situation just discussed, but during most of the evaporation process, the liquid must be anticipated to be in positions that are grossly statically unstable.

5.2. Dynamic Balance

A realistic analysis of evaporation in a capillary of strongly varying bore must therefore consider liquid configurations far from static equilibrium, for instance, such as indicated in Figure 2. A situation is there envisaged such as might be imagined to appear in a snapshot of a "Haines jump" occurring after evaporation has made one meniscus clear a throat. The temperatures and gas pressures at the menisci are still assumed equal, from which it follows that the disparity in meniscus size sets up a pressure gradient propelling the liquid toward the left.

The motion may well be unsteady, and there are two, very small time scales. The shortest is likely to be the liquid column length divided by the speed of sound in it, and the next is the time scale a_t^2/ν ($\sim 10^{-4}$ sec in water, if $a_t \sim 10^{-3}$ cm) of viscous diffusion of shear from the capillary wall

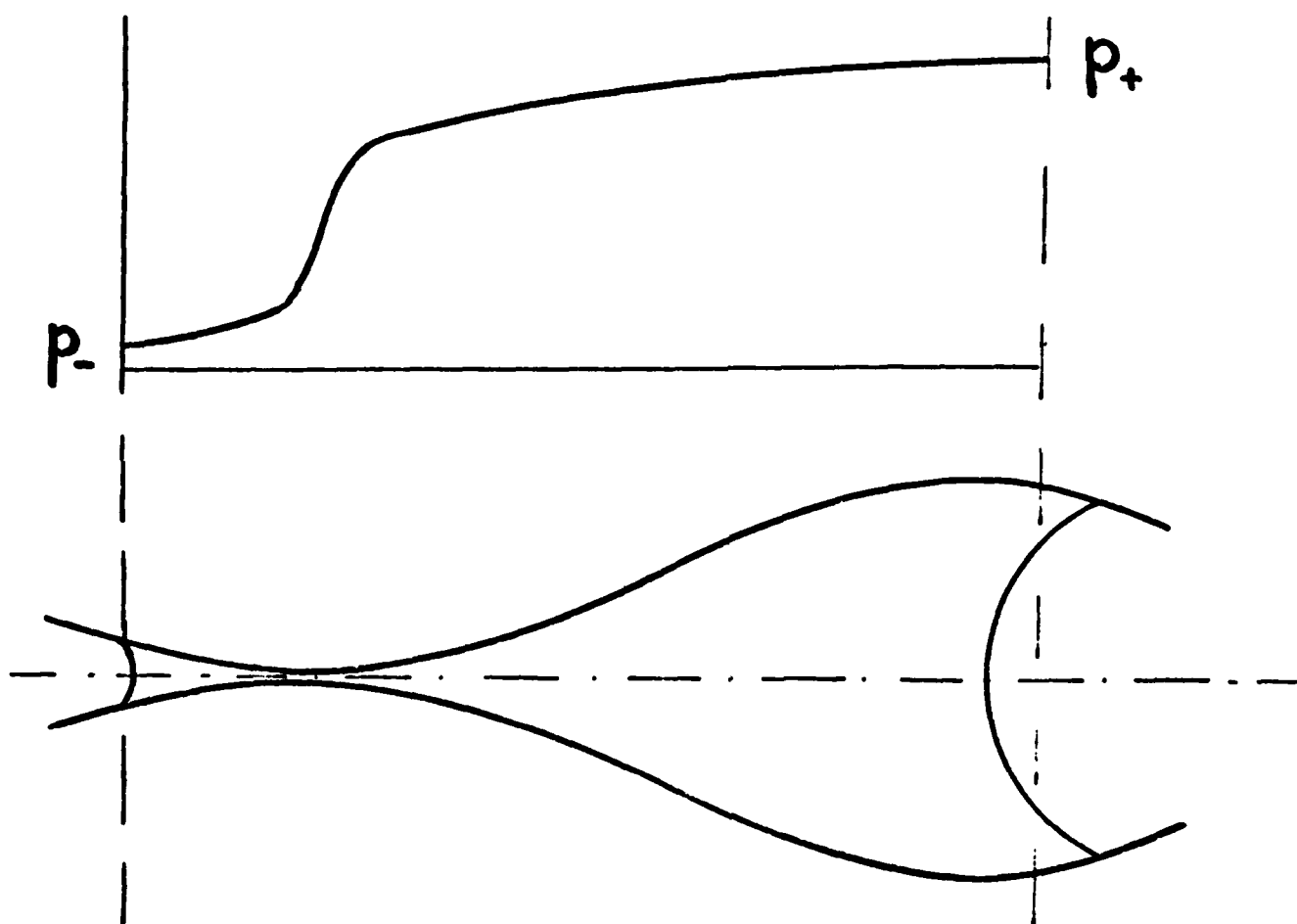


Figure 2

in a throat. The time scales of more direct interest here are much longer and therefore, the point of view of 'quasi-steady' or 'elementary-unsteady' fluid dynamics is called for. The full viscous shear, moreover, may be assumed established in most of the liquid and particularly, throughout the throat. The remarkable degree to which this viscous shear in small capillary throats will be seen presently to control evaporation, provides a vivid illustration of the reason for the prominence of Darcy's Law in fluid motion through porous media.

The liquid-pressure imbalance drives a mass-flow rate $Q(t) < 0$, since the liquid moves toward the smaller meniscus. At the same time, however, the menisci move into the liquid with their respective evaporation velocities $\gamma\kappa/a_+$ and $\gamma\kappa/a_-$ governed by the local thermal process at each meniscus described in Sections 3, 4. In view of the disparity of the meniscus sizes (Figure 2), the first of these relative velocities is small compared with the second, and the gain in clarity achieved by neglecting it will outweigh the loss in accuracy. The larger meniscus, accordingly, is now considered to move just with the velocity $dx_+/dt = Q/(\pi\rho a_+^2)$. The smaller, however, moves with velocity

$$dx_-/dt = \gamma\kappa/a_- + Q/(\pi\rho a_-^2) = u_- . \quad (9)$$

The pressure difference is $p_+ - p_- = 2\sigma/(\alpha_1 a_-)$, by (1) and since a_- is neglected by comparison with a_+ , and the total shear stress is $-8\mu Q l_t/(\pi\rho a_t^4)$, in terms of the "throatlength" l_t defined in the preceding subsection. In small capillaries, liquid inertia cannot play an important role, so that pressure drop and viscous shear cannot be in significant imbalance, and therefore

$$\frac{2\sigma}{\alpha_1 a_-} = - \frac{8\mu Q l_t}{\pi\rho a_t^4} .$$

This is the local version of Darcy's Law relevant to liquid motion ("Haines jump") driven through a small capillary by surface tension at menisci of disparate size. It relates Q to a_- , and (9) may therefore be written

$$a_- u_- = \gamma \epsilon \left[1 - \frac{\sigma a_t^4}{4\gamma\alpha_1 \epsilon \kappa \mu l_t a_-^2} \right].$$

Since $da/dx < 0$ at the position $x = x_-(t)$ of the smaller meniscus in the convergent part of the capillary (Figure 2), (9) now shows the approximate dynamics under present discussion to be represented by an equation of the structure

$$c_1 \frac{d}{dt} (a_-^2) = \frac{c_2}{a_-^2} - 1, \quad c_1 > 0,$$

and with increasing time, a_-^2 must approach

$$c_2 = \sigma a_t^4 / (4\gamma\alpha_1 \epsilon \kappa \mu l_t).$$

This does not correspond to a proper equilibrium because the liquid keeps moving and the pressure drop changes with time, but only a minor drift of the smaller meniscus results therefrom. It remains close to the position x_- such that $a_-^2 = [a(x_-)]^2 = c_2$. In terms of a hybrid capillary number

$$Ct = \epsilon \kappa \mu / (\sigma a_t)$$

based partly on evaporation and partly, on throat radius, then

$$a_-/a_t \sim (4\gamma\alpha_1 Ct l_t/a_t)^{-1/2}.$$

The radius of the smaller meniscus is thus seen to be directly proportional to the square of the throat radius and to depend less strongly on the other factors characterizing capillary geometry, liquid properties and heat supply; the reason for this stems from the dominance of viscous shear in small capillary throats. For a rough impression, for water, $\epsilon = 1/20$ and a throat

radius $a_t = 10^{-3}$ cm, $2 Ct \sim 10^{-5}$, a value 30 for $4\gamma a_1$ is unlikely to be wrong by a large factor, and if $l_t = 20 a_t$, the last formula predicts $a_-/a_t \sim 20$.

The liquid mass-flow rate toward the smaller meniscus then just compensates for the mass-rate of evaporation there. Table 1 (Section 4.2) gives an impression of the corresponding, liquid velocity; for $a_t = 10^{-3}$ cm, e.g., it is only about 10^{-2} cm/sec, and the velocity dx_+/dt of the larger meniscus is still smaller. Most of the evaporation, on the other hand, occurs at the larger meniscus, because its area is larger; by (2), the mass-rate of evaporation there is

$$m = \pi \gamma \rho \kappa \epsilon a_+ = \pi \gamma a_+ \lambda (T_W - T_M) / L . \quad (10)$$

For water and $a_+ = 1$ mm, e.g., it would be about 10^{-7} gr/sec.

In turn, an impression of the dependence of the wall temperature level upon the external heat supply begins to emerge, because the rate Q_h of this supply per meniscus is mL . The smaller of two menisci bounding a liquid column expends relatively less of this, and (10) therefore indicates a rate of external heat supply,

$$mL = \pi \gamma a_+ \lambda (T_W - T_M) ,$$

to a liquid column.

It should be recalled, however, that the simplicity of the predictions in this subsection depends on the assumed disparity of the meniscus sizes. When they are comparable, the more complicated formulae of Section 5.1 must be consulted.

6. VAPOR TRANSPORT

6.1. Open Capillary

For evaporation in dynamic balance, the time-dependence of the processes in the air-vapor mixture (or briefly, the gas) may also be expected to amount to no more than a slow drift leaving the processes quasi-steady. Transfer from the capillary wall will heat the gas from T_M to T_W , but if pressure differences in the gas be still assumed negligible, the attendant density change will amount to only a few percent, at the temperature levels here envisaged. Accordingly, the volume-flow rate, $\pi a^2 u$, of gas will also remain near-constant.

The mass evaporated consists of vapor, but the gas-flow moves the air-vapor mixture and must therefore be accompanied by a diffusion of vapor and air relative to each other. Since the partial vapor density is even smaller than the partial vapor pressure [4], the diffusion of the vapor is governed approximately, by the standard, linear model based on Fick's law $j_v = -\theta \nabla p_v$ for the vapor flux. With unsteadiness already neglected, the same mass-flow rate of vapor must cross every capillary cross-section,

$$\pi a^2 u \rho_v - \pi a^2 \theta dp_v/dx \text{ is independent of } x.$$

Neglect of variations in the volume-flow rate, for a first approximation, reduces this to

$$q \rho_v(x) - dp_v/d\xi = \text{const},$$

where $q^{-1} = \theta/u_m$ is a diffusion-length scale based on the gas velocity u_m at the meniscus and

$$\xi = a_m^2 \int_{x_m}^x [a(s)]^{-2} ds$$

is a modified distance variable. If a subscript e denotes capillary exit

conditions, it follows that

$$\frac{\rho_v - \rho_{vm}}{\rho_{ve} - \rho_{vm}} = e^{q(\xi - \xi_e)},$$

and most of the diffusion is seen to occur within a ξ -distance q^{-1} of the exit, by contrast to the heat transfer, most of which occurs close to the meniscus.

6.2. Vapor Throttling

Matters can be radically different, however, if the gas must pass through a capillary throat. With u denoting again the cross-sectional average of the gas velocity, let subscripts l, g, v, a, m and t distinguish reference to the liquid, gas, vapor, air, gas-side of the meniscus and throat, respectively. Then from the estimate of meniscus velocity relative to the liquid in Section 4.2, $a_m u_m = \gamma \epsilon \mu_l \rho_l / \rho_v$, approximately, and since this is independent of meniscus size, so is the Reynolds number $Re_m = a_m u_m / \nu_a$ of the gas flow at the meniscus. Since $\nu_a \approx 0.15 \text{ cm}^2/\text{sec}$ and $\rho_l / \rho_v \approx 10^3$ for water, the Table 1 (Section 4.2) indicates $Re_m = 2$ to be a typical value.

The mass-flow rate

$$\dot{m} = \pi a^2 u \rho_g \text{ is independent of } x$$

in slow evaporation, and apart from the influence of density changes, the local Reynolds number $Re = au / \nu_a$ of the gas flow varies in proportion to $a_m / a(x)$. For most plausible values of a_m / a_t , the gas-flow therefore remains laminar even in a throat. The pressure drop in the gas flow can then be estimated from Poiseuille's formula,

$$a \, dp/dx = -8 \mu_a \dot{m} / (\pi a^3 \rho_g) = -8 \mu_a a_m^2 u_m / a^3,$$

where $8 \mu_a a_m u_m$ is independent of meniscus size and takes a typical value of $5 \times 10^{-10} \text{ kg}$ when $\mu_a = 2 \times 10^{-10} \text{ kg sec/cm}^2$.

If now $a_m = 10^{-2}$ cm, to fix the ideas, then $a_t/a_m = 1/10$ yields a value of 5×10^{-6} atm for $|a dp/dx|$ at the throat, which indicates insignificant pressure differences in the gas, even if it must pass through several such throats. If $a_t/a_m = 1/100$, however, then the same estimate suggests a value of 5 atm for $|a dp/dx|$ at the throat and clearly, most of the premises and assumptions of this Note collapse: The gas must undergo major gasdynamical effects in its passage through such a throat, the work expended on them must play a major role in the thermodynamical balances, and the meniscus temperature T_M cannot be expected to be close to the initial, ambient temperature T_0 .

The physical nature of evaporation in porous media of sheet-like shape is therefore liable to differ from that in porous media of cube-like or ball-like shape. Evaporation in the latter type may lead soon to a substantial throttling of the gas flow by small throats and hence, to pressure differences in the gas which call for drastic changes in the balances formulated in the preceding sections. The numbers just quoted, moreover, show those pressure differences to be so sensitive to actual capillary-bore sizes that a profitable discussion of evaporation must relate to quite specific geometries and, for this reason, is beyond the scope of this Note.

7. CAPILLARY NETWORKS

In more sheet-like porous media, on the other hand, the great majority of larger capillaries can be expected plausibly to offer escape to the air-vapor mixture without significant pressure drop, and then the earlier discussion provides a basis for thought about evaporation in the irregular network of interconnecting capillaries available to the fluid.

Before evaporation, the liquid fills all the smaller capillary throats and all its menisci are of equal size and are located in positions where the capillaries open out towards the gas (Section 2). Evaporation leaves the gas at the ambient pressure p_0 and the menisci, at the initial temperature T_0 , but changes the position of the liquid. Small menisci remain almost at rest near the smallest throats (Section 5.2), while most of the evaporation occurs at large menisci and makes them move into the liquid, which itself moves towards the smaller menisci. In this way, the larger throats clear first and therefore, the escape of the gas remains relatively unobstructed until most of the liquid has evaporated.

During evaporation, the liquid is not in static equilibrium, but its successive configurations differ in the degree of their static instability. The rapidity of the adjustments, however, depends greatly on the size of passages available to the liquid. Morrow [2] has demonstrated them in a coarse bed of 3 mm balls the relative regularity of which tended to synchronize the more unstable phases. In a bed of 0.1 mm balls, however, throat sizes would have been of the order envisaged in Section 5 for illustration, viscous shear would have been stronger by a factor 10^6 , and adjustments of static instability would have been much harder to observe. Marked instabilities on a larger scale, perhaps related to fingering [6], have also been demonstrated [3] in a coarse, grainy bed.

The present investigation is directed more towards sheet-like porous media in which the solid phase is not grainy, but forms a connected matrix through which the pores thread an irregular network of interconnecting capillaries. That prompts the assumption that small throats are present, and they have been shown to anchor the liquid. If larger throats are connected by passages not obstructed by small throats, relatively rapid Haines jumps must

be anticipated in those passages. If enough small throats are present, however, then 'jumps' become rare and instead, a permanent, very slow 'Haines motion' of the liquid must be anticipated.

In such fine-pored media, it is easier to conjecture an approach to macroscopic predictions from the relations between the temperature levels and the capillary radius, evaporation rate and velocity at individual menisci estimated in Sections 4.2 and 5.2. A knowledge of the statistical distribution of capillary sizes will then permit an estimate to be made of the distribution of capillary radii at menisci, given the mass of liquid still present. In turn, that will determine the distribution of local evaporation rates, given the temperature level in the solid, and that level is then determined by the condition that the total mass-rate of evaporation times the latent heat equals the rate of external heat supply available. At this point of the computation, the capillary-wall temperature T_w has become a known function of the heat supply rate and the liquid mass present, whence the estimates of Sections 4.2 and 5.2 permit us a direct prediction of the instantaneous distribution of evaporation rates and velocities and thereby, the time-development of the distribution of capillary radii at menisci and therefrom in turn, by the same chain of argument, of the time development of the solid temperature level.

In conclusion, the present investigation has concentrated on the local evaporation process and its results emphasize how much the very nature of fluid processes in porous media depend on the specific structure of the medium and particularly, on the distribution of capillary throat sizes.

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APPENDIX

In the context of slow evaporation in a long capillary (Section 4.2), the rates of change of temperature with time, and of capillary radius with distance, become unimportant, and the thermal balance is between heat transfer to, and conduction in, the liquid. The balance (4) then becomes

$$\partial^2 T_\ell / \partial x^2 = (2a_0 h / \lambda) (T_\ell - T_W)$$

if distance is measured in units of the capillary radius a_0 . With $T_W = \text{const.}$ and $T_W - T_\ell(l) = \Delta$, this yields

$$T_\ell(x) - T_W = -\Delta \exp[(2a_0 h / \lambda)^{1/2} (x-l)] .$$

If now the three-dimensional process of steady heat conduction in the liquid with axisymmetric heat transfer from a cylindrical capillary wall be considered, it is governed by Laplace's equation $\nabla^2 T = 0$ for the temperature $T(r, x)$ with boundary condition $T(1, x) = T_W$. The quantity $T_\ell(x)$ of the one-dimensional model is the cross-sectional average of $T(r, x)$.

For constant T_W , the solution is

$$T(r, x) = T_W - \sum c_n J_0(r/\gamma_n) e^{(x-l)/\gamma_n}, \quad J_0(1/\gamma_n) = 0$$

in terms of the Bessel functions of zero order, and the slowest axial decay arises from the first root, $\gamma_1^{-1} = 2.4$. Then on ignoring the c_n for $n > 1$, which depend on the meniscus contact angle,

$$T_\ell(x) = 2 \int_0^1 r T(r, x) dr = T_W - 2c_1 \gamma_1 J_1(1/\gamma_1) e^{(x-l)/\gamma_1} .$$

The rate of heat transfer to the liquid across unit wall area is then

$$(\lambda/a_0) \partial T / \partial r \Big|_{r=1} = (\lambda c_1 / \gamma_1 a_0) J_1(1/\gamma_1) e^{(x-l)/\gamma_1}$$

which equals $h (T_W - T_\ell)$ if $h = \lambda / (2\gamma_1^2 a_0)$, consistently with (6), if $\gamma_h = \gamma_1$.

The most unrealistic feature of this analysis is the uniformity of the capillary wall temperature, which ignores the heat sink that the meniscus represents for the solid. This can be modeled properly only by a consideration of heat conduction in the solid, but a rough estimate can be made as follows. The wall temperature $T(1, \ell)$ at the meniscus will differ from the constant level T_W further away by some fraction $q < 1$ of the amount by which the average $T_\ell(\ell)$ there differs from T_W :

$T_W - T(1, \ell) = q [T_W - T_\ell(\ell)]$. A rough model of the heat sink is then $T_W - T(1, x) = q [T_W - T_\ell(x)]$ for all $x < \ell$. A very similar analysis of Laplace's equation now makes $1/\gamma_1(q)$ the first positive root of $x J_0(x) = 2q J_1(x)$. For instance, $\gamma_1(1/2) \approx 1/2$, by contrast to the earlier value $\gamma_1(0) = 0.4$ found for $T(1, x) = \text{const}$. Clearly, $\gamma_h = \gamma_1 \approx 1/2$ is not very far wrong.

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